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Effects of different drying processes on the concentrations of metals and metalloids in plant materials

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Abstract The drying process of fresh plant materials may affect the porous structure, dehydration and a number of quality characteristics of these materials. Therefore, this study has investigated the effect of different drying processes on the variation of metal and metalloid concentrations in the dried plant materials. Seven varieties of native plant species collected from São Domingos mine were analyzed by instrumental neutron activation analysis (INAA) to investigate the effects of freeze-drying (FD), ambient air-drying (AAD) and oven-drying (OD) process on the concentrations of metals and metalloids in the plant biomass. Comparison of ambient air-dried, oven-dried and freeze-dried preparations allows a phenomenological description of the dehydration artefacts. In the quantitative analysis of metals and metalloids, FD and OD plant samples show the higher concentrations of metals and metalloids when compared to those in the AAD plant biomass. The freeze-drying process is comparatively reliable for determination of metals and metalloids concentrations in plant materials.

Keywords Neutron activation analysis · Drying processes · Plant biomass · Metals and metalloids concentration · Dehydration

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Introduction

Drying treatment of fresh and wet plant samples is essential for the measurement of metals and metalloids. There are different processes of drying treatments, e.g., ambient air-drying (AAD), hot-air-drying (AD), freeze-drying (FD), oven-drying (OD) and vacuum microwave drying (VMD). Thermal damage incurred by a product during drying is directly proportional to the temperature and time involved. The high temperature and long drying time during drying process often causes heat damage and adversely affects texture, color, flavor and nutritional value of products [1, 2]. By contrast, freeze drying can protect heat damage and produce products with excellent structural retention; however, it is a costly process when compared with ambient air-drying but similar to oven-drying and vacuum microwave drying process. Moreover, the absence of air during freeze drying may inhibit oxidation, redox-sensitive changes of metals and therefore, color and nutrient content of biological products can be largely preserved.

Wang et al. [3] investigated the effects of different drying methods on the surface wettability of wood strands and reported that the surface polar energies of oven-dried pine strands and rotating drum-dried poplar strands were higher than on strands dried by microwave and air-drying methods. The porous structure of dehydrated plant materials (apple, potato, cabbage, and carrot) is a key parameter that affects the transport properties and a number of quality characteristics of these materials. The freeze drying resulted in the very high bulk porosity and larger pore size of plant materials, while a gradual involvement of air drying resulted in a decreasing porosity and smaller pore size, due to the collapse of structure in air dried plant materials during dehydration. The shrinkage of the material followed the evaporation of water; however, the porosity was developed especially

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during the last stages of drying. The surface areas of freeze dried samples were of the order of 1 m^2/g, which is typical value for dehydrated foodstuffs [4].

A number of analytical methods are currently available for the determination of elements in soil, plant and water samples, directly from the dissolved analyte, such as atomic absorption spectrophotometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS). However, the solubilization procedures are complicated and time-consuming, and information on the chemical forms may become lost along the process. By contrast, instrumental neutron activation analysis (INAA) is non-destructive and quite useful to determine trace elements. There are a plenty of studies that used INAA for the analysis of metals and metalloids in plant samples [5–8].

The different drying processes that are currently applied for the drying of fresh plant species and determination of metals and metalloids, may result in some variations in the concentrations of chemical elements in dried plant materials. As for example, after washing with deionized water, Kassem et al. [7] dried the leaves of some plant species (olive, eggplant, alfalfa and cabbage) at 25 °C in a clean fume hood, then ground and determined trace elements in plants in the Orontes basin of Syria by using instrumental neutron activation analysis (see other references therein). Freitas et al. [5] washed the lichen samples with de-ionized water and oven-dried at 40 °C for 24 h for the preparation of a lichen reference material. By contrast, Freitas et al. [6] and Vieira et al. [8] followed the freeze drying process: the plant leaves were fast frozen in a deep freezer and subsequently freeze dried for 2 days in a laboratory freeze dryer and then ground in Teflon (balls and capsule) mills for 10 min, which together with the sample had been immersed before in liquid nitrogen for 2 min. However, to the authors' best knowledge there is no study, conducted yet, on the effect of different drying processes on the variations of concentrations of chemical elements in the plant biomass. Which process is more accurate and reliable has not yet been studied. Therefore, the main objective of this study was to investigate the effect of freeze-drying process on the concentrations of metals and metalloids in plant biomass as compared to conventional ambient air-drying and oven-drying processes. The different plant species collected from a mining contaminated area were used in this investigation.

Materials and methods

Samples preparation

The five different plant species were sampled from four sampling sites of São Domingos copper sulfide mine that is located in south-east Portugal [6], one of a number of volcanogenic massive sulphide deposits within the Iberian Pyrite Belt (northern sector; 37°38′00–37°40′30 N, 7°19′05–7°20′05 W). All the fresh plant samples were washed three times by tap water and deionized water to remove dead tissue and extraneous material (large soil particles, litter, bugs) in the laboratory, and then they were split into constituent parts—roots, stems, leaves, flowers. The leaves of plant samples were divided into three parts. One portion of samples was processed for air-drying, another for oven drying and the other for freeze drying.

Air drying of plant materials

The air drying of plant leaves was performed in summer time open air (May 2009) at ambient temperature (av. 20 °C) with 70% relative humidity (annual average). The samples were fully air dried for about 2 weeks.

Oven drying of plant materials

The plant leaves were air-dried like above and subsequently oven-dried at 65 °C for 4 days. Ground leaf samples were re-dried at 85 °C for ≥24 h to remove any moisture adsorbed by the sample during the grinding process.

Freeze drying of plant materials

For freeze drying, the plant leaves were fast frozen in a deep freezer and subsequently freeze dried for 2 days in a laboratory freeze dryer.

Analysis of metals and metalloids

Detailed field and laboratory procedures for handling, preparing—sorting, cleansing, pelletizing—and analyzing plant samples have been previously described [6, 8]. All air-dried, oven-dried and freeze-dried plant samples were ground in Teflon™ (balls and capsule) mills, which was carefully cleaned between samples. The sample powder was thoroughly homogenized, and made into 250-mg pellets for neutron activation analysis, following the k_0-standardized procedure. All elemental determinations were carried out at the Portuguese Research Reactor of the Technological and Nuclear Institute (RPI-ITN, Sacavém; maximum nominal power: 1 MW). The sample pellets were irradiated for 5 h at thermal neutron fluxes of 2.25×10^{12} cm^{-2} s^{-1} for long irradiations, together with one disc (thickness: 125 μm; diameter: 5 mm) of an Al—0.1% Au alloy as comparator. Gamma spectra were acquired on a liquid N_2-cooled, ORTEC®-calibrated, high-purity Ge detector (1.85 keV resolution at 1.33 MeV; 30%

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Table 1 Mean concentrations of different elements and their counting statistics' uncertainties (unc.%) in air-dried plant samples collected from mining area (mg/kg, dry weight)

Sample	Plant species	As	Unc. (%)	Fe	Unc. (%)	La	Unc. (%)	Sb	Unc. (%)	Sc	Unc. (%)	Zn	Unc. (%)
S1	*Lavandula luisieri* L.	4.80	14.4	816	12.4	0.30	9.9	0.75	11.1	0.09	12.1	188	13.8
S1	*Cistus ladanifer* L.	5.66	12.7	311	12.3	0.23	11.2	0.93	13.5	0.07	11.7	35	11.2
S1	*Daphne gnidium* L.	6.38	8.4	456	4.3	0.07	14.2	0.80	11.9	0.11	9.2	53	7.8
S1	*Erica australis* L.	10.35	7.1	100	4.9	0.05	12.7	0.28	13.7	0.02	12.7	10	13.2
S2	*Daphne gnidium* L.	1.94	14.3	187	7.7	0.16	13.6	0.32	12.7	0.03	12.7	68	10.7
S2	*Cistus ladanifer* L.	4.79	11.2	326	9.3	0.24	14.6	0.82	7.5	0.08	14.5	43	14.2
S2	*Ulex eriocladus* L.	11.62	2	551	4	0.31	2.7	2.43	3.2	0.11	2.6	32	5.8
S2	*Lavandula luisieri* L.	4.95	4.1	189	11.2	0.19	5.2	0.25	10.8	0.05	6.1	85	2.5
S3	*Daphne gnidium* L.	7.32	8.1	384	8	0.09	11.9	1.32	7.4	0.04	14.1	53	14.5
S3	*Lavandula luisieri* L.	5.09	12.2	623	8.8	0.33	13.8	0.78	9.6	0.09	8.2	178	13.5
S3	*Daphne gnidium* L.	2.15	7.5	150	12.5	0.14	9.1	0.27	14.6	0.03	11.3	12	8.8
S4	*Erica australis* L.	10.52	13.9	99	4.5	0.05	14.3	0.61	12.7	0.03	8.7	9	9.5
S4	*Ulex eriocladus* L.	11.74	1.8	539	4	0.29	2.4	2.3	2.8	0.11	2.7	32	11.5
S4	*Lavandula luisieri* L.	4.85	3.8	224	5.5	0.18	5.6	0.27	11.7	0.05	12	85	3.5

Table 2 Mean concentrations of different elements and their counting statistics' uncertainties (unc.%) in freeze-dried plant samples collected from mining area (mg/kg, dry weight)

Sample	Plant species	As	Unc. (%)	Fe	Unc. (%)	La	Unc. (%)	Sb	Unc. (%)	Sc	Unc. (%)	Zn	Unc. (%)
S1	*Lavandula luisieri* L.	7.26	6.3	949	7.4	0.46	7.5	1.50	5.1	0.15	2.7	324	4.3
S1	*Cistus ladanifer* L.	6.84	5.5	323	11.7	0.24	11.8	0.59	8.8	0.09	11.1	151	5.3
S1	*Daphne gnidium* L.	8.48	6.6	743	11.4	0.06	9.5	0.31	11.4	0.02	14.9	83	4.7
S1	*Erica australis* L.	12.88	2.7	736	6.4	0.38	7.2	2.93	3.3	0.17	3.0	25	5.6
S2	*Daphne gnidium* L.	4.07	8.5	194	9.2	0.12	14.4	0.32	9.1	0.05	0.0	153	5.5
S2	*Cistus ladanifer* L.	5.12	13.7	367	14.6	0.29	11.3	0.75	8.7	0.09	11.3	142	5.5
S2	*Ulex eriocladus* L.	14.55	3.9	651	7.2	0.37	6.6	0.98	5.1	0.09	4.8	36	6.1
S2	*Lavandula luisieri* L.	6.87	8.4	297	11.9	0.23	5.4	0.66	9.7	0.08	9.2	97	4.1
S3	*Daphne gnidium* L.	7.78	8.2	428	13.0	0.09	3.8	0.29	9.5	0.06	8.3	79	4.7
S3	*Lavandula luisieri* L.	6.85	4.3	716	7.8	0.45	7.4	1.01	9.8	0.14	4.3	327	2.9
S3	*Daphne gnidium* L.	4.18	10.2	183	11.0	0.13	5.1	0.35	13.1	0.04	15.0	166	4.5
S4	*Erica australis* L.	12.73	3.2	672	4.4	0.35	5.3	2.85	3.3	0.18	3.1	25	8.6
S4	*Ulex eriocladus* L.	15.47	5.5	668	6.7	0.35	6.5	0.95	5.0	0.08	8.8	36	13.2
S4	*Lavandula luisieri* L.	5.23	8.6	304	12.7	0.30	13.4	0.39	9.7	0.09	6.0	107	8.2

relative efficiency). Samples were measured after 4 days and 4 weeks (long irradiations). The comparator was measured after 1 week (long irradiations). Elemental concentrations were assessed through the k_0-IAEA program (version 3.21). Quality control was asserted by analyzing certified reference materials (IAEA-336 lichen) concurrently with the field samples. Deviations from certified values were generally within 1–15%.

Results and discussion

The concentrations of As, Fe, La, Sb, Sc and Zn in the ambient air-dried samples of plant species *Lavandula luisieri* (L), *Daphne gnidium* (L), *Cistus ladanifer* (L), *Erica australis* (L), *Ulex eriocladus* (L) and *L. luisieri* (L) are shown in Table 1. The concentrations of Fe, and Zn are higher compared to those of As, Sb, La, and Sc. The concentrations of above metals and metalloids in freeze-dried and oven-dried plant materials are shown in Tables 2 and Table 3, respectively. The results demonstrate that the concentrations of As, Fe, La, Sb, Sc and Zn in freeze-dried plant materials showed the highest values and were relatively higher than those in ambient air-dried plant samples (Fig. 1a–c; Tables 1, 2), but were almost similar to those in oven-dried plant materials (Fig. 1a–c; Tables 2, 3). Only a few samples exhibited the exceptions where the oven-dried plant materials showed the higher values of elements than

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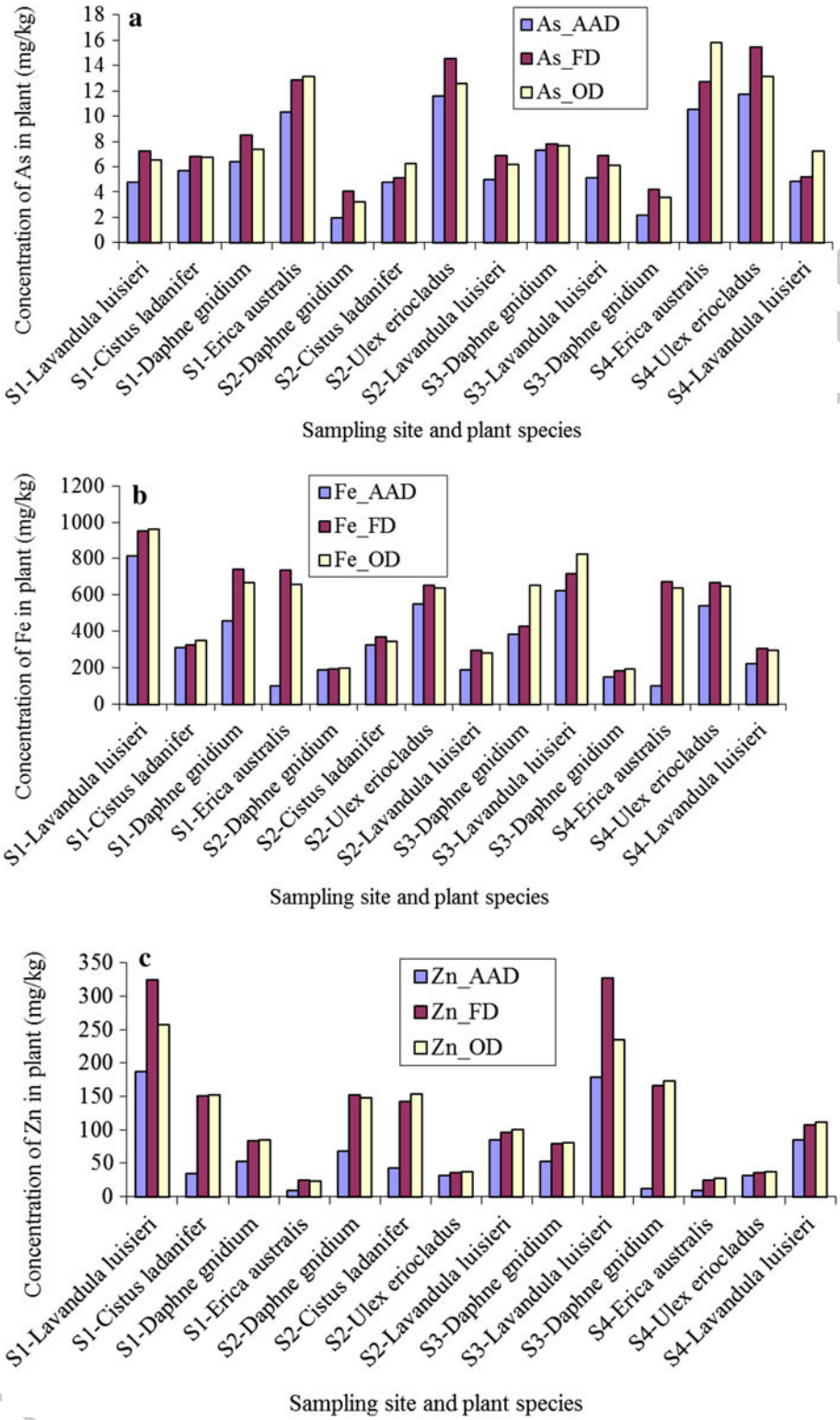

Fig. 1 Comparative distributions of selected chemical elements (arsenic—As, iron—Fe, and zinc—Zn) in ambient air-dried (AAD), freeze-dried (FD) and oven-dried (OD) plant samples of different species (mg/kg)

those of others. These results suggest that the uses of FD and AAD process for the drying and analysis of metals and metalloids in the same plant samples do not produce the same results. The lower concentrations of metals and metalloids in the ambient air-dried plant samples may occur due to high moisture content and less dehydration

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Table 3 Mean concentrations of different elements and their counting statistics' uncertainties (unc.%) in oven dried (at 65 °C) plant samples collected from mining area (mg/kg, dry weight)

Sample	Plant species	As	Unc. (%)	Fe	Unc. (%)	La	Unc. (%)	Sb	Unc. (%)	Sc	Unc. (%)	Zn	Unc. (%)
S1	*Lavandula luisieri* L.	6.54	7.3	962	8.7	0.47	9.10	1.20	2.6	0.14	4.60	257	5.4
S1	*Cistus ladanifer* L.	6.71	8.4	348	10.6	0.27	12.3	0.72	8.8	0.08	11.1	152	3.2
S1	*Daphne gnidium* L.	7.35	3.4	668	9.5	0.05	11.5	0.30	11.4	0.02	14.2	85	6.3
S1	*Erica australis* L.	13.11	4.5	657	5.2	0.37	8.3	2.81	3.3	0.15	4.8	23	6.8
S2	*Daphne gnidium* L.	3.26	9.2	200	8.9	0.14	14.4	0.31	12.7	0.03	12.3	148	4.4
S2	*Cistus ladanifer* L.	6.25	12.2	344	11.6	0.28	11.5	0.75	8.7	0.07	10.5	153	5.7
S2	*Ulex eriocladus* L.	12.56	4.9	636	8.3	0.39	7.9	0.95	5.1	0.08	5.7	38	5.8
S2	*Lavandula luisieri* L.	6.17	6.4	280	10.1	0.26	15.0	0.63	10.3	0.06	9.7	101	4.9
S3	*Daphne gnidium* L.	7.68	7.5	652	12.3	0.08	11.4	0.29	13.6	0.05	10.4	81	3.5
S3	*Lavandula luisieri* L.	6.12	8.1	824	7.4	0.49	7.7	1.30	9.8	0.14	4.3	235	3.6
S3	*Daphne gnidium* L.	3.61	9.7	191	9.7	0.15	14.6	0.34	12.4	0.04	15.0	173	5.9
S4	*Erica australis* L.	15.78	5.4	639	5.8	0.34	5.8	2.82	3.3	0.16	3.1	27	7.4
S4	*Ulex eriocladus* L.	13.12	5.7	647	5.2	0.38	7.9	0.92	6.4	0.09	9.5	37	12.5
S4	*Lavandula luisieri* L.	7.25	3.7	295	11.8	0.28	11.5	0.31	9.9	0.09	5.3	112	7.2

effects. The ambient air-drying process is a relative one that depends on the humidity and temperature of the environment of that locality. The same plant samples processed in the different ambient air-drying conditions in different countries can produce the different results; and it is difficult to mention how much the variations in results will occur in different conditions at this moment that require further study. Furthermore, the air temperature varies depending on seasons of the year (e.g., summer, fall, winter, spring etc.). The degree of temperature, and time duration of AAD process have variable significant effects on the drying of plant biomass. By contrast, the FD and OD are the controlled processes those can be applied at controlled conditions in any season of the year.

The freeze-drying is a much faster drying process than ambient air drying and oven-drying. While FD takes only 2–3 days, AAD and OD processes require several days to dry the plant materials for grinding into powder. The freeze-dried plant materials have higher porous structure and the lowest density than AAD plant samples, since this process allows ice to sublime, leaving voids within the structure [9]. Therefore, when the AAD and FD plant samples are weighed to the same amount and measured by INAA for determination of different metals and metalloids, the two drying processes produce the different results for the same plant samples of the same weight. During the hot air drying and oven drying processes, some elements can be volatilized (e.g. Hg). Out of these three processes, the ambient air drying process is the easiest one. The results of this study infer that selection of drying process is important for the analysis of environmental samples. Arsenic concentrations in the FD plant samples increased by av. 23.67% compared to those in the AAD plant samples. Similar trends of increase for the other metals and metalloids were found for the FD samples when compared with the AAD samples.

Conclusion

The concentrations of metals and metalloids in the freeze-dried plant biomass showed the highest values, and were relatively higher than those in the ambient air-dried plant materials, but almost similar with the concentrations found in the oven-dried plant samples. This trend of metal and metalloid concentrations were generally found for all the plant species collected from the contaminated mining area; and a few variations in this trend were also observed. Given the advantages, and disadvantages of the three drying processes (AAD, FD and OD), the freeze-drying process is considered to be more controlled and reliable method for determination of metals and metalloids in some plant materials.

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